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(54) Preparation of sulphonic fluorinated polymer solutions

(57) A process for preparing a solution and/or dispersion containing sulphonic (per)fluorinated ionomers having -SO₃M functional groups, wherein M is selected from H, Li, Na, K, NR₄ (R equal to or different from each other are selected from H, CH₃, C₂H₅), characterized in that it dissolves the above defined ionomers at a temperature comprised between the room temperature and about 150°C, in a monophasic ternary mixture essentially constituted by water, by a C₁-C₄ alcohol and by a fluoro(poly)oxyalkylene having one hydrogen atom in at least a fluorinated end group; the dispersed polymer particle sizes are in the range 30-100 nm.

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Description

[0001] The present invention relates to a process for preparing fluorinated polymer solutions at low temperature having sulphonic functional groups and to liquid compositions obtainable from said process.

5 [0002] Specifically, the invention relates to solutions obtainable with a process in which a temperature between the room temperature and about 150°C, preferably between 50°C and 100°C, is used. The liquid compositions obtainable from said process are stable solutions and/or dispersions wherein the particle sizes, determined by dynamic laser light scattering (DLS), are in the range 30-100 nm, preferably 40-70 nm, the distribution being monomodal. The invention liquid compositions contain an amount of fluorinated polymers having sulphonic functional groups (ionomers) ranging from about 0.5% and about 30% by weight. The equivalent weight of said fluorinated polymer is in the range of about 400-1300, preferably between 650-800 nm, still more preferably between 730-795 nm.

[0003] The preparation of solutions and/or dispersions of sulphonic (per)fluorinated ionomers having different equivalent weight (EW) is known in the art.

[0004] As equivalent weight, the polymer weight in acid form necessary to neutralize a NaOH equivalent is meant; the equivalent weight is determined by polymer titration in the acid form with a standard NaOH solution.

15 [0005] GB 1,286,859 describes ionomer dispersions having equivalent weight not higher than 1060 using an aqueous solution containing at least 5% by weight of an organic solvent. As organic solvents primary, secondary and tertiary C₁-C₄ alcohols; amides such as dimethylacetamide, dimethylformamide; acetone, etc., are mentioned. The used organic solvent feature is to have a boiling point lower than 130°C such that they are easily removable after polymer casting and a solubility in water of at least 5% by weight. The temperatures used in the examples for the dissolution process are comprised between the room temperature and 100°C.

[0006] Tests carried out by the Applicant have shown that by the process described in said patent, the dispersed particle sizes are in the range of about 150-300 nm. As it is well known, as the particle size increases, the polymer concentration being equal, the specific surface decreases. Therefore sizes of this order limit the sulphonic group availability on the particle surface and therefore reduce the ionomer efficiency in all those applications where a high presence of such groups is required, as in the case of impregnation treatments on porous supports, for example of PTFE or ceramic materials.

[0007] Dissolution processes with hydroalcoholic mixtures at temperatures higher than at least 180°C and up to 350°C for ionomers having equivalent weights higher than about 1000, are also known.

30 [0008] See for example USP 4,433,082 which describes a dissolution process in a liquid medium of ionic exchange (per)fluorinated polymers having -SO₃M functional groups, wherein M is H, Na, K having an equivalent weight in the range 1025-1500. Water, optionally containing alcohols, is used. A mixture constituted by 20-90% by weight of water and by 10-80% by weight of an alcohol (C₁-C₄) and/or other solvents miscible in water in a dissolution temperature range from 180 to 300°C, preferably from 210°C to 250°C, is for example mentioned. Such dissolution is carried out for at least 0.5 h in a closed vessel obtaining two liquid phases having a different density, wherefore it is necessary to separate the phase having a lower density from the one containing the polymer.

[0009] The disadvantage of this process is to operate at high temperatures leading to corrosion of the used containers (autoclaves). For this reason the used materials are special steels, e.g. Hastelloy. Also in this case it is however necessary a surface treatment since the corrosion takes place all the same even though in longer times.

40 [0010] In the publication by R.B. Moore, III, C.R. Martin, *Macromolecules* 22, 3594-3599 of 1989 the dissolution conditions for sulphonic perfluorinated ionomers having an equivalent weight in the range of about 600-1300 are reported. Also in this case the polymer is dissolved in hydroalcoholic mixtures and it is pointed out that the temperature necessary to dissolve the sulphonic perfluorinated ionomers changes with the used ionomer equivalent weight. It is meaningful to note that also for the ionomers having equivalent weight lower than 1000 the dissolution method requires the use of high operating temperatures, always higher than 240°C, and of dissolution times higher than one hour.

[0011] Patent Application WO 98/16581 relates to a dissolution process at high temperature (150-350°C) to obtain solutions and/or dispersions comprising sulphonic perfluorinated ionomers. The dispersion medium is substantially water, free of alcohols. An example is reported wherein the dissolution of a sulphonic copolymer TFE/perfluoro(3-oxa-4-pentenesulphonylfluoride) in -SO₃H form having an equivalent weight lower than 800 at a temperature of 230°C for 5 hours under stirring, is shown. Besides, a dissolution method in a non aqueous medium constituted by alcohols and/or organic solvents miscible in water is described. Also in this case it is necessary to operate at temperatures in the range 150°C-350°C. According to this patent at least 25% of the polymer particles have a size in the range of about 2-30 nm, determined by low angle X rays measurements.

55 [0012] Experiments carried out by the Applicant (see the Examples) have shown that the distribution is bimodal, wherein at least 50% of the particle distribution is about 120 nm. Therefore also in this case the same disadvantages described for GB 1,286,859 are present.

[0013] In the mentioned patents, the high temperature required to obtain the sulphonic (per)fluorinated ionomer dissolution in a dispersion medium involves the use of autoclaves constituted by special corrosion-resistant materials, as

described in patent WO 98/16581, thus determining an increase of the plant costs. When not valuable steels are used, corrosion problems and consequent pollution of the final solution from the metals constituting the autoclave take place, making it not very suitable to be used in all the applications where an high purity, for instance in electrolytic and fuel cells, is required.

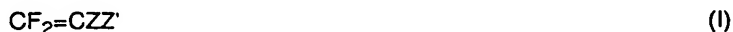
[0014] The need was felt to have available solutions and/or dispersions of ionomers obtainable by a process which does not require high temperatures, preferably without the use of equipments under pressure (autoclaves) and contemporaneously allows to obtain the dispersed polymer particle sizes in the range 30-100 nm, preferably 40-70 nm. As said, the particle size reduction involves an increase of the respective specific surface, the dispersed polymer concentration being equal, with consequent result improvement in impregnation, casting, etc. applications.

[0015] The Applicant has surprisingly and unexpectedly found that it is possible to solubilize sulphonic (per)fluorinated ionomers in suitable solvent mixtures at low temperature contemporaneously obtaining particles having sizes in the above indicated range, overcoming the above mentioned disadvantages of the prior art.

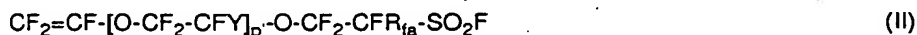
[0016] An object of the present invention is a process to prepare a solution and/or dispersion containing sulphonic (per)-fluorinated ionomers having $-SO_3M$ functional groups, wherein M is selected from H, Li, Na, K, NR_4 (R equal to or different from each other are selected from H, CH_3 , C_2H_5), preferably H, characterized in that it dissolves the ionomers above defined at a temperature comprised between the room temperature and about $150^\circ C$, preferably between $50^\circ C$ and $100^\circ C$, in a monophasic ternary mixture essentially constituted by water in a percentage in the range 0.1%-50% by weight, by a C_1 - C_4 alcohol in a percentage in the range 50%-99% by weight and by a fluoro(poly)oxyalkylene having one hydrogen atom in at least a fluorinated end group, preferably in both terminals, in a percentage in the range 0.1%-40% by weight; wherein the dispersed polymer particle sizes, determined by dynamic laser light scattering (DLS), are in the range 30-100 nm, preferably 40-70 nm, the distribution being monomodal.

[0017] Another object of the invention are liquid compositions obtainable from the above mentioned process comprising a (per)fluorinated ionomer amount in the range 0.5%-30% by weight, having equivalent weight from about 400 to 1300, preferably between 650-800, still more preferably 730-795, and dispersed particle sizes in the range 30-100 nm, preferably 40-70 nm.

[0018] The present invention sulphonic (per) fluorinated ionomers are obtained by the polymerization of a monomer having structure (I) with a monomer having structure (II):

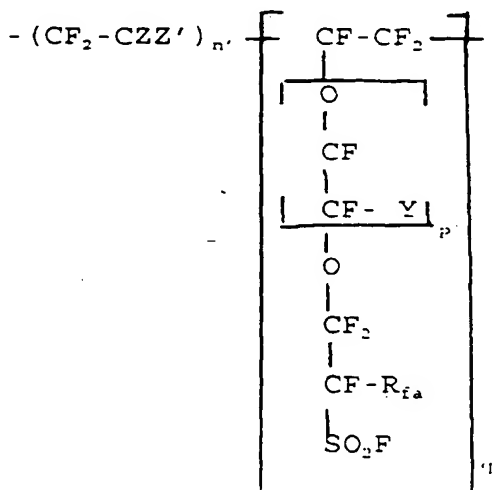


wherein: Z and Z' are independently selected from H, Cl, F, CF_3 , preferably they are F.



wherein: Y is selected from F, CF_3 ; R_{fa} is selected from F, Cl, C_1 - C_4 perfluoroalkyl group, preferably it is F; p' is an integer selected from 0,1,2, preferably it is 0.

[0019] From the polymerization, (per)fluorinated sulphonic copolymers are obtained having the following repeating units:



wherein: Z, Z', Y, R_{1a}, p' have the above defined meaning; n' is an integer in the range 1-15, q' is an integer in the range 1-10, n'/q' is in the range 1-10 and the ionomer equivalent weight is in the range of about 400-1300, preferably between 650-800, still more preferably between 750-795.

[0020] After the polymerization, the -SO₂F fluorosulphonic groups conversion in ionic form is necessary before proceeding to the polymer dissolution in the monophasic ternary mixture of the present invention. The conversion requires alkaline hydrolysis to obtain the -SO₃M form where M is selected from Li, Na, K, NR₄ (R=H, CH₃, C₂H₅), and optional subsequent acid hydrolysis to obtain the -SO₃H form. The acid form -SO₃H is preferred.

[0021] The preferred ternary mixture used for the ionomer dissolution is constituted by water in a percentage in the range 5-20% by weight, by a C₁-C₄ primary alcohol in a percentage in the range 65%-85% and by a fluoro(poly)oxyalkylene having hydrogenated terminals, with a boiling temperature in the range 80°C-120°C, in a percentage in the range 5%-25% by weight.

[0022] Ternary mixtures of the mentioned components show a ternary diagram characterized by a wide monophasic zone wherein the three components form limpid and stable solutions as shown in the patent USP 5,654,263 in the name of the Applicant, herein incorporated by reference.

[0023] The existing zone width of such monophasic can even considerably change in connection with the type of the used alcohol and fluoro(poly)oxyalkylene, particularly in connection with the boiling temperature and the hydrogen content. At any rate, for the skilled in the field, it is sufficient to carry out some mixing tests of the three components to identify the monophasic existing zone.

[0024] According to a not binding theory, the Applicant deems that the introduction of the fluorinated component [fluoro-(poly)oxyalkylene] in the solvent mixture allows an effective solvation of the ionomer hydrophobic fluorinated part which, combined to the salvation of the ionomer polar part through the mixture hydroalcoholic component, brings to an improved macromolecule solubilization and therefore a dispersed aggregate size reduction. This is possible thanks to the formation of a single phase comprising both the hydrophobic fluorinated part and the two hydrophilic hydrogenated components.

[0025] The effect caused by the introduction of the fluorinated compound in the solvent mixture seems to destructurize the ionic clusters formed by the ionomeric macromolecules, thus allowing a reduction in the particle size. Experiments carried out by the Applicant have shown that, being constant the ratio between water and alcohol in the monophasic of the invention, a gradually increase of the hydroperfluoropolyether leads to a decrease of the size of the ionic clusters. This effect was completely unexpected in view of the prior art.

[0026] The particle size distribution obtained by dissolving the ionomer in the monophasic of the invention is surprisingly and unexpectedly monomodal.

[0027] A further advantage of the process of the present invention with respect to the prior art resides in the fact that no separation step of the organic phase is required. In fact with the dissolution process of the present invention only one phase is obtained.

[0028] From the industrial point of view this is a relevant simplification of the industrial process.

[0029] The process of the present invention comprises the dissolution of a sulphonic (per)fluorinated ionomer amount ranging from about 0.5% to about 30% by weight in the above defined monophasic ternary mixture at a temperature lower than about 150°C for about 2 hours. The obtained solutions are limpid and transparent and with an increasing growing viscosity as the ionomer concentration increases. In order to verify the solution stability they are subjected to ultracentrifugation to speed up the particle sedimentation process. With the invention process it has been found that by ultracentrifugation no substantial ionomer separation is noticed.

[0030] As said, the dissolution temperatures can range from the room one up to about 150°C in connection with the equivalent weight of the ionomer to be dissolved. As sulphonic (per)fluorinated ionomers the ones having low equivalent weight and those having high equivalent weight up to about 1300 can be used.

[0031] In order to obtain the monophasic ternary mixture used in the present invention the following alcohols: methanol, ethanol, n-propanol, isopropanol, butanol isobutanol, etc. can be used; primary alcohols such as methanol and propanol are preferably used.

[0032] In order to obtain the monophasic ternary mixture used in the present invention fluoropolyoxyalkylenes comprising one or more repeating units, statistically distributed along the chain, selected from:

-CFZO-, -CF₂CFZO-, -CF₂CF(CF₃)O-, -CF(CF₃)O-, -CZ₂CF₂CF₂O-, -CF₂CF(OR_b)O-, -CF(OR_b)O- can be used, wherein Z is -H or -F; R_b is -CF₃, -C₂F₅, or -C₃F₇; and by hydrogenated end groups selected from -CF₂H, -CF₂CF₂H, -CFH-CF₃, and -CFH-OR_b, wherein R_b is defined as above, or perfluorinated end groups selected from -CF₃, -C₂F₅, and -C₃F₇, at least one of the end groups containing one hydrogen atom. One or more of the fluorine atoms of the terminal end can be substituted by chlorine.

[0033] The average molecular weight of the above mentioned fluoropolyoxyalkylenes is such that the boiling range, at the pressure of 1 atm, is generally in the range 25°-200°C, preferably 50°-150°C, more preferably 80°-120°C.

[0034] Specifically, fluoropolyoxyalkylenes containing at least one hydrogen atom in the end groups as above defined, can be selected from the following classes:

(a) $T_1-O(CF_2-CF(CF_3)O)_a(CFXO)_b-T_2$

wherein:

T_1 and T_2 , equal to or different from each other, are $-CF_2H$, $-CFH-CF_3$ hydrogenated groups, or $-CF_3$, $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated; X is $-F$ or $-CF_3$; a/b is in the range 5-15;

(b) $T_3-O(CF_2CF_2O)_c(CF_2O)_d-T_4$

wherein:

T_3 and T_4 , equal to or different from each other, are $-CF_2H$ or $-CF_2-CF_2H$ hydrogenated groups, or $-CF_3$, $-C_2F_5$ perfluorinated groups, at least one of the end groups being hydrogenated, preferably both; c/d is in the range 0.3-5;

(c) $T_5-O(CF_2-CF(CF_3)O)_e(CF_2CF_2O)_f(CFXO)_g-T_6$

wherein:

T_5 and T_6 , equal to or different from each other, are $-CF_2H$, $-CF_2CF_2H$, or $-CFH-CF_3$ hydrogenated groups, or $-CF_3$, $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated; X is $-F$ or $-CF_3$; $e/(f+g)$ is in the range 1-10, f/g is in the range 1-10;

(d) $T_7-O(CF_2-CF(CF_3)O)_h-T_8$

wherein:

T_7 and T_8 are $-CPU-CF_3$ hydrogenated groups, or $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated;

(e) $T_9-O(CZ_2CF_2CF_2O)_i-T_{10}$

wherein:

Z is F or H ; T_9 and T_{10} , equal to or different from each other, are $-CF_2H$ or $-CF_2-CF_2H$ groups, or $-CF_3$, $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated;

(f) $T_{11}-O(CF_2O)_j(CF_2CF(OR_{fb})O)_k(CF(OR_{fb})O)_l-T_{12}$

wherein:

R_{fb} is $-CF_3$, $-C_2F_5$, or $-C_3F_7$; T_{11} and T_{12} , equal to or different from each other, are $-CF_2H$, $-CF_2CF_2H$, $-CFH-OR_{fb}$ groups, or $-CF_3$, $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated; $k+l$ and $j+k+l$ are at least equal to 2, $k/(j+l)$ is in the range 10^{-2} - 10^3 , $1/j$ is in the range 10^{-2} - 10^2 ;

(g) $T_{13}-O(CF_2-CF(CF_3)O)_m(CFXO)_n(CFHO)_o(CF_2CFHO)_p-T_{14}$

wherein:

T_{13} and T_{14} , equal to or different from each other, are $-CF_2H$, $-CFH-CF_3$ hydrogenated groups, or $-CF_3$, $-C_2F_5$, $-C_3F_7$ perfluorinated groups, at least one of the end groups being hydrogenated; X is $-F$ or $-CF_3$; m/n is in the range 5-40, $m/(o+p)$ is in the range 2-50, $o+p$ is at least 3, or is lower than p ;

(h) $T_{15}-O(CF_2CF_2O)_q(CF_2O)_r(CFHO)_s(CF_2CFHO)_t-T_{16}$

wherein:

T_{15} and T_{16} , equal to or different from each other, are $-CF_2H$, $-CF_2-CF_2H$ hydrogenated groups, or $-CF_3$, $-C_2F_5$ perfluorinated groups, at least one of the end groups being hydrogenated; q/r is in the range 0.5-2, $(q+r)/(s+t)$ is in the range 3-40, $s+t$ is at least 3, s is lower than t ;

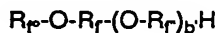
(i) $T_{17}-O(CF_2-CF(CF_3)O)_u(CF_2CF_2O)_v(CFXO)_w(CFHO)_x(CF_2CFHO)_y-T_{18}$

wherein:

T_{17} and T_{18} , equal to or different from each other, are $-CF_2H$, $-CF_2CF_2H$, $-CFH-CF_3$ hydrogenated groups, or

-CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; X is -F or -CF₃; (u+v)/w is in the range 5-40, (u+v)/(x+y) is in the range 2-50, x+y is at least 3, x is lower than y.

[0035] The fluoropolyoxyalkylenes which can be used in the monophasic ternary mixture used in the present invention preferably have general formula:



wherein R_p, R_f, R_f equal to or different from each other are linear or branched perfluoroalkyls having from 1 to 12 C atoms; b' is an integer from 0 to 4, preferably 0 or 1; R_p can contain one hydrogen atom on the chain end carbon.

[0036] The following compounds can be mentioned as examples: C₈F₁₇-O-C₂F₄H, C₇F₁₅-O-C₂F₄H, C₆F₁₃-O-C₂F₄-O-CF₂H, C₄F₉-O-C₂F₄H, HC₂F₄-O-C₂F₄-O-C₂F₄H, C₄F₉-O-(CF₂)₅H.

[0037] The above fluorooxyalkylenes are known and are described in the patent WO 95/32174. Other preferred fluorooxyalkylenes have general formula:



wherein R_p has the above mentioned meaning and R_h is a linear or branched hydrogenated alkyl having from 1 to 10 C atoms. The preferred compound is the one in which R_p=C₄F₉ and R_h=CH₃.

[0038] The end groups of the above mentioned fluoro(poly)oxyalkylenes can optionally contain one Cl atom instead of one F atom.

[0039] The solutions obtainable at low temperature by the invention process can be used in the preparation of ionic exchange membranes used in fuel cells and in electrolytic processes.

[0040] The present invention will be now further illustrated from the following working examples, which cannot in any way limit the scope of the invention itself.

EXAMPLES

Characterization

Dynamic Laser Light Scattering (DLS) analysis

[0041] An argon laser having a wave length of 514.5 nm with a 300 mW power so as to measure the size of the aggregates present in the solution. The dynamic method is based on the recording of an autocorrelation curve correlating the scattering intensity and the relaxation time of the scattering particles. It is thus possible to draw a Γ relaxation rate, which is proportional to the D diffusion coefficient of the scattering species:

$$\Gamma = D \cdot q^2$$

where q represents the wave vector which is expressed as follows:

$$q = (4\pi n / \lambda) \sin(\theta/2)$$

where n is the medium refractive index, λ is the wavelength and θ is the scattering angle at which the measurements are determined.

[0042] The D diffusion coefficient is related to the diameter of the scattering particles by the Stokes-Einstein equation:

$$D = kT / 3\pi\eta\phi$$

wherein K is the Boltzmann constant, T the temperature, η the medium viscosity and ϕ the diameter of the particles.

[0043] The so described method is applicable to diluted solutions to avoid multiple scattering effects due to the signal overlapping.

[0044] In the examples the concentration of 1% by weight of ionomer was used.

EXAMPLE 1

[0045] A solution at 1% by weight of sulphonic ionomer obtained by polymerizing tetrafluoroethylene (TFE) with CP₂=CFOCF₂CF₂-SO₂F, converted in -SO₃H form and having equivalent weight (EW) equal to 770, was prepared by

dissolution of the same in a ternary mixture constituted by H₂O (7.3% by weight), n-propanol (71% by weight) and one fluoropolyoxyalkylene (21.7% by weight) having the formula:



with boiling range from 120°C to 180°C and average molecular weight equal to 500. Such dissolution was carried out in a glass container equipped with magnetic stirring in which the temperature is controlled by thermostatic bath. After 2 hours at 70°C the solution was ultracentrifuged at 22,000 rpm. for 1 hour and no presence of any precipitate was noticed.

EXAMPLE 2

[0046] A solution at 10% by weight of sulphonic ionomer obtained by copolymerizing TFE with CF₂=CFOCF₂CF₂SO₂F, converted in -SO₃H form and having EW=770, was prepared by dissolution of the same in a ternary mixture constituted by H₂O (15% by weight), methanol (80%) and a fluoropolyoxyalkylene (5%) having the formula:



with boiling range between 80°C and 120°C and number average molecular weight equal to 350. Such dissolution was carried out in a glass container equipped with magnetic stirring wherein the temperature is controlled by thermostatic bath. After 24 hours at 50°C the solution was completely transparent and the Brookfield viscosity measured at 25°C, was 24 cP. The dynamic laser light scattering (LS) analysis showed a dispersed aggregate size of about 70 nm. A narrow monomodal distribution was observed.

[0047] The so obtained solution was deposited on a flat PTFE support by a stratifying knife having nominal thickness of 15 mils; after the solvent evaporation a transparent, homogeneous and continuous membrane, lacking of evident defects (mud cracks, holes), was obtained.

[0048] The optical microscopy and the Scanning Electron Microscopy (SEM) showed that the film surface was continuous and without the above mentioned defects.

EXAMPLE 3

[0049] A solution at 10% by weight of sulphonic ionomer obtained by copolymerizing TFE with CF₂=CFOCF₂CF₂SO₂F, converted in -SO₃H form and having EW=770, was prepared by dissolution of the same in a ternary mixture constituted by H₂O (9.4% by weight), methanol (69%) and a fluoropolyoxyalkylene (21.6%) having the formula:



with boiling range between 120°C and 180°C and number average molecular weight equal to 500. The solution was put in a closed autoclave at 150°C. After 3 hours stirring was stopped and the autoclave was cooled. The solution was perfectly transparent and had a dry content equal to 9.5% by weight and a Brookfield viscosity at 25°C equal to 55 cP. The dynamic laser light scattering (DLS) analysis showed a dispersed aggregate size of about 40-50 nm. A narrow monomodal distribution was observed.

EXAMPLE 4

[0050] A solution at 1% by weight of sulphonic ionomer obtained by copolymerizing TFE with CF₂=CFOCF₂CF₂SO₂F, converted in -SO₃H form and having EW=770, was prepared by dissolution of the same in a ternary mixture constituted by H₂O (9.4% by weight), methanol (69%) and a fluoropolyoxyalkylene (21.6%) having the formula:



with boiling range between 120°C and 180°C and number average molecular weight equal to 500. Such dissolution was carried out in a glass container equipped with magnetic stirring wherein the temperature is controlled by thermostatic bath. After 2 hours at 70°C the solution was ultracentrifuged at 22,000 rpm. for 1 h and no presence of any precipitate was noticed. The dynamic laser light scattering (DLLS) analysis showed a dispersed aggregate size of about 30 nm. A narrow monomodal distribution was observed.

EXAMPLE 5 (comparative)

[0051] A solution at 1% by weight of sulphonic ionomer obtained by copolymerizing TFE with $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$, converted in $-\text{SO}_3\text{H}$ form and having $\text{EW}=770$, was prepared by dissolution of the same in a binary mixture constituted by water and methanol in the same relative ratios of Example 3 (H_2O 12% by weight, methanol 88%). Such dissolution was carried out in a glass container equipped with magnetic stirring wherein the temperature is controlled by thermostatic bath. After 2 hours at 70°C the solution was ultracentrifugated at 22,000 rpm. for 1 h and no presence of any precipitate was noticed. The dynamic laser light scattering (DLS) analysis showed a dispersed aggregate size of about 150 nm.

EXAMPLE 6

[0052] Example 2 has been repeated but using a sulphonic ionomer having $\text{EW} = 730$.
 [0053] The results obtained are similar to those of Example 2.

EXAMPLE 7

[0054] Example 2 has been repeated but using a sulphonic ionomer having $\text{EX} = 750$.
 [0055] The results obtained are similar to those of Example 2.

EXAMPLE 8

[0056] Example 2 has been repeated but using a sulphonic ionomer having $\text{EW} = 790$.
 [0057] The results obtained are similar to those of Example 2.

EXAMPLE 9 (comparative)

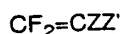
[0058] A solution was made by adding in a shaker tube 7.0 g. of the sulphonic ionomer having $\text{EW} = 778$ to 50 ml of water and 15 ml of toluene. The mixture was heated to 230°C for 5 hours with shaking. The vessel was allowed to cool to ambient temperature and the organic layer separated from the aqueous layer. The aqueous layer contained 11.5% of dry polymer and had a viscosity of 2 cP.

[0059] The DLLS analysis showed a bimodal aggregate size distribution: the first distribution centered at: a size of 23 nm and the second centered on a size of 123 nm.

Claims

1. A process for preparing a solution and/or dispersion containing sulphonic (per)fluorinated ionomers having $-\text{SO}_3\text{M}$ functional groups, wherein M is selected from H, Li, Na, K, NR_4 (R equal to or different from each other are selected from H, CH_3 , C_2H_5), preferably H, characterized in that it dissolves the above defined ionomers at a temperature comprised between the room temperature and about 150°C , preferably between 50°C and 100°C , in a monophasic ternary mixture essentially constituted by water in a percentage in the range 0.1%-50% by weight, by a C_1 - C_4 alcohol in a percentage in the range 50%-99% by weight and by a fluoro(poly)oxyalkylene having one hydrogen atom in at least a fluorinated end group, preferably in both end groups, in a percentage in the range 0.1%-40% by weight; wherein the dispersed polymer particle sizes, determined by dynamic laser light scattering (DLLS), are in the range 30-100 nm, preferably 40-70 nm.

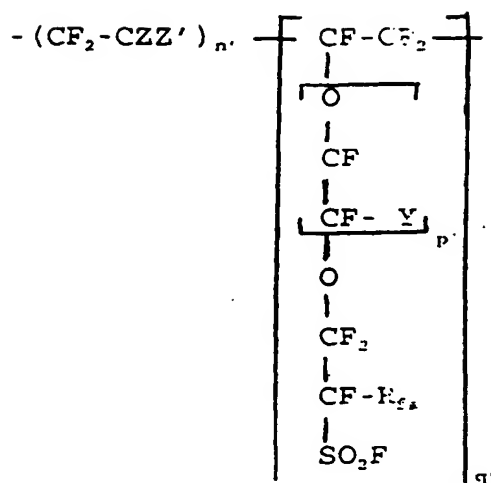
2. A process according to claim 1 wherein the sulphonic (per) fluorinated ionomers are obtained by polymerization of a monomer having structure (I) with a monomer having structure (II):



wherein: Z and Z' are independently selected from H, Cl, F, CF_3 , they preferably are F.



wherein: Y is selected from F, CF_3 ; R_{1a} is selected from F, Cl, C_1 - C_4 perfluoroalkyl group, it preferably is F; p' is an integer selected from 0,1,2, it is preferably 0; obtaining perfluorinated sulphonic copolymers having the following repeating units:



wherein: Z, Z', Y, R_{fa}, p' have the above defined meaning; n' is an integer in the range 1-15, q' is an integer in the range 1-10, n'/q' is in the range 1-10 and the ionomer equivalent weight (EW) is in the range of about 400-1300; and by the subsequent conversion of the -SO₂F fluorosulphonic groups in the -SO₃M ionic form wherein M is selected from H, Li, Na, K, NR₄ (R=H, CH₃, C₂H₅).

3. A process according to claims 1 and 2 wherein the ternary mixture is constituted by water in a percentage in the range 5-20% by weight, by a C₁-C₄ primary alcohol in a percentage in the range 65%-85% and by a fluoro(poly)-oxyalkylene having hydrogenated terminals and boiling temperature in the range 80°C-120°C, in a percentage in the range 5%-25% by weight.
4. A process according to claims 1-3 wherein the amount of sulphonic perfluorinated ionomer ranges from about 0.5% to about 30% by weight.
5. A process according to claims 1-4 wherein alcohol is selected among methanol, ethanol, n-propanol, isopropanol, butanol, isobutanol; preferably methanol and n-propanol.
6. A process according to claims 1-5 wherein fluoropolyoxyalkylenes are constituted by one or more repeating units, statistically distributed along the chain, selected from:
 -CFZO-, -CF₂CFZO-, -CF₂CF(CF₃)O-, -CF(CF₃)O-, -CZ₂CF₂CF₂O-, -CF₂CF(OR_{fb})O-, -CF(OR_{fb})O-
 wherein Z is -H or -F; R_{fb} is -CF₃, -C₂F₅, or -C₃F₇; and by hydrogenated end groups selected from -CF₂H, -CF₂CF₂H, -CFH-CF₃, and -CFH-OR_{fb}, wherein R_{fb} is as above defined, or perfluorinated end groups selected from -CF₃, -C₂F₅, and -C₃F₇, at least one of the end groups containing one hydrogen atom;
 said fluoropolyoxyalkylenes having an average molecular weight such that the boiling range, at the pressure of 1 atm, is generally in the range 25°-200°C, preferably 50°-120°C.
7. A process according to claim 6 wherein the fluoropolyoxyalkylenes are selected from the following classes:

(a) T₁-O(CF₂-CF(CF₃)O)_a(CFXO)_b-T₂
 wherein:

T₁ and T₂, equal to or different from each other, are -CF₂H, -CFH-CF₃ hydrogenated groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; X is -F or -CF₃; a/b is in the range 5-15;

(b) T₃-O(CF₂CF₂O)_c(CF₂O)_d-T₄
 wherein:

T₃ and T₄, equal to or different from each other, are -CF₂H or -CF₂-CF₂H hydrogenated groups, or -CF₃,

-C₂F₅ perfluorinated groups, at least one of the end groups being hydrogenated, preferably both; c/d is in the range 0.3-5;

(c) T₅-O(CF₂-CF(CF₃)O)_e(CF₂CF₂O)_f(CFXO)_g-T₆

wherein:

T₅ and T₆, equal to or different from each other, are -CF₂H, -CF₂CF₂H, or -CFH-CF₃ hydrogenated groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; X is -F or -CF₃; e/(f+g) is in the range 1-10, f/g is in the range 1-10;

(d) T₇-O(CF₂-CF(CF₃)O)_h-T₈

wherein:

T₇ and T₈ are -CFH-CF₃ hydrogenated groups, or -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated;

(e) T₉-O(CZ₂CF₂CF₂O)_i-T₁₀

wherein:

Z is F or H; T₉ and T₁₀, equal to or different from each other, are -CF₂H or -CF₂-CF₂H groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated;

(f) T₁₁-O(CF₂O)_j(CF₂CF(OR_{fb})O)_k(CF(OR_{fb})O)_l-T₁₂

wherein:

R_{fb} is -CF₃, -C₂F₅, or -C₃F₇; T₁₁ and T₁₂, equal to or different from each other, are -CF₂H, -CF₂CF₂H, -CFH-OR_{fb} groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; k+l and j+k+l are at least equal to 2, k/(j+l) is in the range 10⁻²-10³, l/j is in the range 10⁻²-10²;

(g) T₁₃-O(CF₂-CF(CF₃)O)_m(CFXO)_n(CFHO)_o(CF₂CFHO)_p-T₁₄

wherein:

T₁₃ and T₁₄, equal to or different from each other, are -CF₂H, -CFH-CF₃ hydrogenated groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; X is -F or -CF₃;

m/n is in the range 5-40, m/(o+p) is in the range 2-50, o+p is at least 3, or is lower than p;

(h) T₁₅-O(CF₂CF₂O)_q(CF₂O)_r(CFHO)_s(CF₂CFHO)_t-T₁₆

wherein:

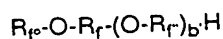
T₁₅ and T₁₆, equal to or different from each other, are -CF₂H, -CF₂-CF₂H hydrogenated groups, or -CF₃, -C₂F₅ perfluorinated groups, at least one of the end groups being hydrogenated; q/r is in the range 0.5-2, (q+r)/(s+t) is in the range 3-40 s+t is at least 3, s is lower than t;

(i) T₁₇-O(CF₂-CF(CF₃)O)_u(CF₂CF₂O)_v(CFXC)_w(CFHO)_x(CF₂CFHO)_y-T₁₈

wherein:

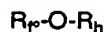
T₁₇ and T₁₈, equal to or different from each other, are -CF₂H, -CF₂CF₂H, -CFH-CF₃ hydrogenated groups, or -CF₃, -C₂F₅, -C₃F₇ perfluorinated groups, at least one of the end groups being hydrogenated; X is -F or -CF₃; (u+v)/w is in the range 5-40, (u-v)/(x+y) is in the range 2-50, x+y is at least 3, x is lower than y.

8. A process according to claims 1-5 wherein the fluoroxyalkylenes have the formula:



wherein R_f, R_f, R_f equal to or different from each other are linear or branched perfluoroalkyls having from 1 to 12

C atoms; R_p can contain one hydrogen atom on the chain end carbon;
 b' is an integer from 0 to 4, preferably 0 or 1;
 or they have the formula:



wherein R_p has the above mentioned meaning and R_h is a linear or branched hydrogenated alkyl having from 1 to 10 C atoms, preferably $R_p=C_4F_9$ and $R_h=CH_3$.

9. A process according to claims 1-8 wherein the fluoro(poly)oxyalkylene end groups can optionally contain one Cl atom instead of one F atom.
10. A process according to claims 1-9 wherein the EW is comprised between 650-800, preferably 730-795.
11. Liquid compositions obtainable according to claims 1-10 comprising a perfluorinated ionomer amount in the range 0.5-30% by weight, having equivalent weight from about 400 to 1300, preferably 650-800, more preferably 730-795 and dispersed particle sizes in the range 30-100 nm, preferably 40-70 nm.